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Author(s):	Cooper, Michael William Donald Stanek, Christopher Richard Andersson, Anders David Ragnar
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Milestone Report: Calculate parameters controlling grain growth in doped UO_2

[M3MS-18LA0201035]

M. W. D. Cooper, C. R. Stanek, D. A. Andersson

Materials Science and Technology Division, Los Alamos National Laboratory P.O. Box 1663, Los Alamos, NM 87545, USA

Abstract

The safe and efficient operation of nuclear reactors depends upon accurate fuel performance modeling. By understanding the underlying mechanisms that govern fuel properties fuel performance codes can be improved and new fuels can be developed. Additives have been added to UO_2 during sintering to increase grain size with the aim of reducing fission gas release and increasing pellet plasticity. We have used atomistic simulations to calculate the defect chemistry of UO_2 doped with Cr, Al, Mn, Fe, V, Ti, and Mg. A common mechanism has been revealed for dopant solution as positively charged interstitials in UO_2 . An apparent preference of the interstitial site for low valence cations means that dopants with chemistry that enables charge states of 1+ or 2+ (Cr, Mn, Fe, V, Ti, and Mg) are accommodated at concentrations sufficiently high to modify the host defect concentrations. Conversely, the low solubility of Al at the interstitial site is attributed to its inability to access 1+ or 2+ charge states, instead remaining 3+. Dopants that are accommodated in significant quantities as interstitials correlate well with dopants that have been observed experimentally to enhance grain growth. In response to the solution of dopants as positively charged interstitials, the negatively charged uranium vacancy concentrations are increased. The increase in the uranium diffusivity that would result from this is proposed as the responsible mechanism for enhanced grain growth. The defect concentrations calculated from atomistic simulations have been parametrized for use in longer length and timescale simulations that will be used to simulate grain growth under sintering conditions and fission gas release.

1. Introduction

Due to its radiation tolerance, high melting point, and chemical stability UO_2 has been widely studied as the most common nuclear reactor fuel. Fission gas release causes technical issues for reactor operation. The thermal conductivity of the fuel-cladding gap is degraded and the fuel rod pressure increased by fission gas release. Dopants have been used during pellet sintering to promote grain growth, with the objective of increasing the distance travelled

Email address: cooper_m@lanl.gov (M. W. D. Cooper)

(and time taken) during the rate limiting intra-granular diffusion step before rapid fission gas release from the grain boundaries. An additional benefit of large grains is increased plasticity and thermal creep, which reduces mechanical interactions between the pellet and the metal cladding [1–3]. Several dopants, Cr [4–11], Nb [12–14], Mg [14–16], Ti [14, 17], and V [18], have been identified as UO_2 grain enlargers.

Although liquid phase sintering, due to the CrO eutectic, has been identified in the literature as the primary mechanism for enhanced grain growth [4–9], Bourgeois *et al.* [4] measured an increase in grain size as a function of Cr content even when the sintering temperature was below the CrO eutectic melting temperature (1950 K [19]). In the same paper Bourgeois *et al.* [4] show there is a peak in grain size at the Cr solubility limit [4]. While liquid phase sintering is the mechanism for enhanced grain size if Cr content is well in excess of the solubility limit (when temperatures are above the eutectic point), the underlying atomic processes that determine the solution based mechanism near the solubility limit are poorly understood. Observations similar to that of Bourgeois *et al.* [4] on Cr-doped UO_2 have also been made for Ti-doped UO_2 [17]. For ideal grain growth, grain boundary kinetics are proportional to self-diffusion and it is under this assumption that the discussion of our results is based. Uranium self-diffusion proceeds by a vacancy mediated mechanism making the availability of uranium vacancies important for grain boundary kinetics.

Atomistic simulations are well placed to investigate solution based mechanisms for enhanced grain growth. Mechanisms by which Cr in solution can affect grain growth have often been dismissed due to its assumed preference for the 3+ charge state and substitution of a U^{4+} . This would create negatively charged dopant defects reducing the concentration of the similarly-charged uranium vacancies and suppressing uranium diffusivity leading to a reduction in uranium mass transport. The presence of dopants as positively charged interstitials has been suggested in the literature [20–22], however it is not seen in previous atomistic simulations [20, 23, 24], which predict the negatively charged substitutional defect to be dominant.

The previous atomistic work was based on Cr^{3+} , thus motivating our extended investigation by relaxing this assumption so that Cr may occupy the 1+, 2+, 3+, 4+, 5+, or 6+ charge states. In a previous milestone report [25], we showed that the ability of Cr to access low valence states enabled its accommodation as an interstitial species. Formation of positively charged Cr interstitials resulted in an increase in the uranium vacancy concentration at sintering temperatures and was proposed as the mechanism for enhanced grain growth in Cr-doped UO_2 . On the other hand, Al accommodation at the interstitial was far less favourable due to its 3+ charge state. Comparison of Al with Cr highlighted that chemistry enabling low charge states is preferential for dopant interstitial formation. In particular, the presence of *d* electrons in the outer shell for Cr means it has a number of charge states that are similar in energy. We use this hypothesis to extend the analysis to other dopants that may exhibit suitable chemistry: the transition metals (Ti, V, Mn, and Fe) and the group 2 metal, Mg. The results of this work have been published in Ref. [26] and for the convenience of the reader the contents of this paper have been appended to this milestone report (see Appendix). Here we provide a summary of the key results from Ref. [26] and also parametrize these results into a form suitable for use in mesoscale simulations

and fuel performance codes.

2. Methodology

Energy minimization using interatomic forces calculated from density functional theory (DFT) has been used to calculate defect energies in UO_2 . For computational efficiency defect vibration entropies were calculated from the phonon density of states predicted using the Busker potential [27]. The DFT defect energies and empirical potential vibrational entropies have been used to determine the defect free energy, which is used to determine the defect concentrations in doped UO_2 that satisfy charge neutrality as a function of oxygen partial pressure and temperature. For a much more detailed description of methodological details the reader is referred to Ref. [26] (see Appendix). Since the previous milestone two modifications have been made to the methodology. The vibrational entropy of the solid oxide phases (e.g. Cr_2O_3 , CrO and UO_2) have been added to the free energy of defect formation and the entropy associated with the change in defect volume due to different defect charge states has been accounted for.

3. Results and Discussion

Defect concentrations for UO_2 doped with Cr, Al, Ti, V, Mn, Mg, and Fe have been predicted as a function of temperature for fixed oxygen partial pressure. These full results have been published in Ref. [26] (see Appendix), where a more detailed discussion can be found. The key findings from that work are:

- A common mechanism was identified for the accommodation of dopants at interstitial sites in UO_2 at high temperatures, whereby low charge states (below 3+) were more favourably accommodated.
- Dopants with chemistry that allows them to access charge states of less than 3+ were able to be accommodated more favourably, leading to high dopant interstitial concentrations.
 - Transition metal dopants Cr, Ti, V, Mn, and Fe could readily access 1+ or 2+ charge states leading to high interstitial concentrations.
 - The group 2 metal Mg was found to be accommodated with high interstitial concentrations.
 - The group 3 metal Al remained in its most favoured 3+ charge state and interstitial doping was suppressed.
- In all cases where high interstitial concentrations were predicted, the extrinsic positive charge caused an increase in the concentration of all negatively charged defects and a decrease in the concentrations of all positively charged defects.
- The increase, with respect to undoped UO_2 , in the concentration of negatively charged uranium vacancies (which govern uranium diffusivity) was proposed as the underlying

mechanism for the increase in grain growth kinetics, as seen experimentally for several of these dopants (Cr [4–11], Mg [14–16], Ti [14, 17], and V [18]). In particular, for Cr-doped UO_2 we believe this mechanism explains the peak in grain size observed at the solubility limit as a function of Cr wt. % [4]. Increased uranium vacancy concentrations will also increase densification rates during sintering. An alternative interpretation of these results in terms of grain growth is that as the dopants go into solution with UO_2 they modify the grain boundary energies in a way that enhances reorientation growth mechanisms.

- Enhanced uranium vacancy concentrations could increase fission gas diffusivity at high temperatures potentially leading to an increase in fission gas release during reactor operation.
- The modifications to the methodology since the previous milestone have resulted in higher predictions of the uranium vacancy concentrations and the 1+ charge state replacing the 2+ charge state as the most favourable for the Cr interstitial. Similarly, V, Mn, and Fe also exhibit 1+ charge states at the interstitial site. On the other hand, the Ti interstitial prefers a 2+ charge state because the loss of an additional electron allows it to empty its d electron sub-shell.

Our predictions of defect concentrations in UO_2 doped with various species can be implemented in phase-field simulations of grain growth and sintering, as well as fission gas release models in fuel performance codes. To support this, analytical expressions have been fitted to the relative stability of dopant defects (see Ref. [26] and Appendix) and in this report to the uranium vacancy concentrations, as follows.

There are three distinct temperature regimes to which three Arrhenius functions can be fitted as a function of temperature. The range of temperatures over which a regime exists is determined by the dominant charge compensating defect. Taking Cr doped UO_2 as an example, at low temperatures the dominant charge compensating defects are v_{U}''' and $\text{U}_{\text{U}}^{\bullet}$, for intermediate temperatures U_{U}' and $\text{U}_{\text{U}}^{\bullet}$ dominate, and for high temperatures the dopant itself, $\text{Cr}_{\text{U}}^{\bullet}$, and U_{U}' dominate. Mn, Ti, V, and Fe all behave in a similar way, such that the transition between the low and intermediate regimes is independent of the dopant and occurs at the same temperature (1130 K), however the transition from the intermediate to the high temperature regime is dependent on the solubility of a given dopant. The uranium vacancies for Al and undoped UO_2 are identical because $\text{Al}_{\text{U}}^{\bullet\bullet\bullet}$ is never a dominant defect. Mg, on the other hand, replaces v_{U}''' as the dominant negatively charged defect in the low temperature regime. The resulting transition to the intermediate (U_{U}' and $\text{U}_{\text{U}}^{\bullet}$ dominated) regime now occurs at 1430 K for Mg-doped UO_2 .

Figure 1 shows an Arrhenius plot of the v_{U}''' concentrations for undoped and Cr-doped UO_2 . At low and intermediate temperatures the Cr solubility is too low to affect $[v_{\text{U}}''']$, such that it is identical for the undoped and Cr-doped cases. This is true for all dopants studied other than Mg, which is the only dopant to have significant solubility at low temperatures. In the high temperature regime $[v_{\text{U}}''']$ is higher for doped UO_2 compared to undoped and separate

Arrhenius functions are fitted.

$$[v_U'''] = A \exp \frac{-B}{k_B T} \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, and A and B are fitted to the $[v_U''']$ data. Table 1 shows the parameters from fitting Arrhenius functions (equation 1) to $[v_U''']$ in undoped and (Cr, Mn, Fe, Al, Mg, Ti, V)-doped UO_2 . Any longer length and timescale simulations that use uranium vacancy concentration as an input can readily implement these parameters to investigate the effect that enhanced uranium vacancies might have in doped fuel. The parameters have, as such, been distributed to collaborators within NEAMS for implementation in modeling of grain growth, sintering and fission gas release.

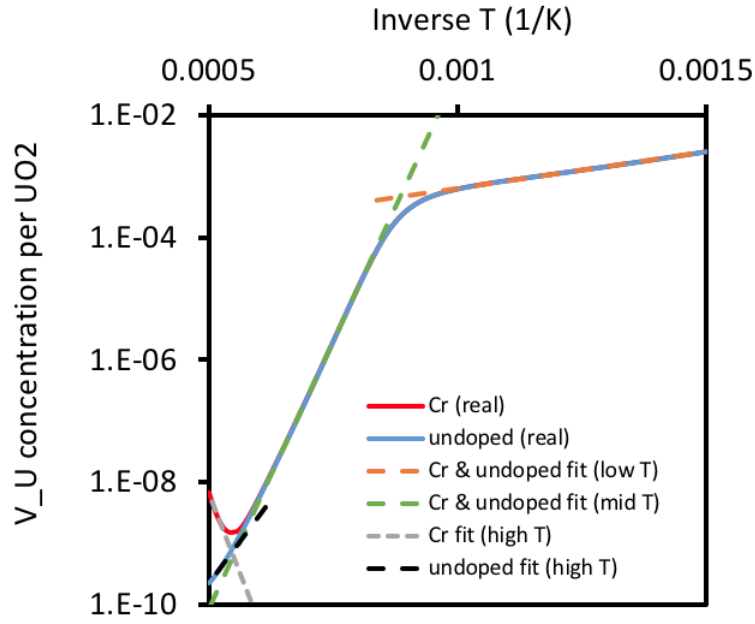


Figure 1: An Arrhenius plot of the v_U''' concentrations for undoped UO_2 (solid blue line) and Cr-doped UO_2 (solid red line). For each plot there are three regimes to which four Arrhenius functions (dashed lines) have been fitted to: low temperature (same for Cr-doped and undoped), intermediate temperature (same for Cr-doped and undoped), and Cr-doped high temperature and undoped high temperature.

4. Conclusions

We have tested the hypothesis discussed in the previous milestone [25] that the interstitial site in UO_2 has a preference for low charge state cations and, therefore, dopant chemistry that enables low charge states, without a significant energy penalty, will be favourable. Extension of the defect analysis shows that for several transition metals and the group 2 metal Mg, concentrations of 1+ and 2+ charged interstitials are sufficiently high at sintering temperatures to alter

Table 1: Parameters for the Arrhenius functions ($A \exp \frac{-B}{k_b T}$) fitted to the data for $[v_U''']$ over three temperature regimes for doped and undoped UO_2 (see example for Cr in Figure 1).

Dopant, X, and Temperature range	A (no units)	B (eV)
Low temperature regime		
600 K to 1130 K for undoped and Cr, Mn, Fe, Al, Ti, V doped	3.926×10^{-5}	-0.240
600 K to 1468 K for Mg-doped	2.845×10^{-9}	-0.313
Intermediate temperature regime		
1130 K to (low limit of high T regime) for undoped and Cr, Mn, Fe, Al, Ti, V doped	1.426×10^{-19}	-3.480
1468 K to 1937 K for Mg-doped	8.892×10^{-16}	-2.208
High temperature regime		
1775 K to 2000 K for undoped and Al-doped	7.964×10^{-16}	-2.161
1822 K to 2000 K for Cr-doped	1.832×10^2	4.155
1776 K to 2000 K for Mn-doped	1.754×10^4	4.657
1878 K to 2000 K for Fe-doped	2.174×10^{-3}	2.174
1788 K to 2000 K for Ti-doped	1.896×10^{-3}	2.297
1755 K to 2000 K for V-doped	1.272×10^{11}	6.948
1937 K to 2000 K for Mg-doped	7.443×10^{-8}	0.863

the concentration of host uranium and oxygen defects. In particular, uranium vacancy concentrations are significantly enhanced for all dopants that could access charge states lower than 3+ (Cr, Mn, Fe, Ti, V, and Mg). The increased uranium diffusivity associated with enhanced uranium vacancy concentrations is proposed as the responsible mechanism for the large grains observed in UO_2 doped with Ti, Mg, Cr, or V. Conversely, we propose that because Al does not exhibit charge states other than 3+ it will not result in significant interstitial concentrations and will not exhibit the associated increase in grain size. This is consistent with experimental observations of small grains for Al-doped UO_2 [21]. In order to make a better comparison with experiment the results from atomistic simulations have been parametrized for implementation in mesoscale simulations of grain growth and densification during sintering, as well as fission gas release modeling.

Appendix A. Unformatted contents from: MWD Cooper, CR Stanek, DA Andersson, "The role of dopant charge state on defect chemistry and grain growth of doped UO₂", *Acta Materialia* 150, 403-413 (2018)

Appendix A.1. Abstract

Additives are widely used to control the microstructure of materials via their effect on defect chemistry during sintering. As the primary nuclear fuel, the properties of UO₂ are crucial for safe and efficient reactor operation. UO₂ has been manipulated by fuel vendors through doping to enhance grain size to provide improved fission gas retention and plasticity. In this work the common phenomenon that governs the effect of Mg, Ti, V, Cr, Mn, and Fe doping of UO₂ for enhanced grain growth is revealed, elucidating experimental observations. A combined density functional theory and empirical potential description of defect free energy is used to calculate the doped UO₂ defect concentrations as a function of temperature. At high (sintering) temperatures all dopants studied transition to a positively charged interstitial defect. Furthermore, a number of dopants (Ti, V, Cr, and Mn) do so in sufficiently high concentrations to greatly increase the negatively charged uranium vacancy concentration. High uranium vacancy concentrations can enhance grain growth and fission gas diffusion. Mg and Fe also enhance uranium vacancy concentrations but to a lesser extent, while Al has no impact. The enhanced uranium vacancy concentrations, associated with solution of dopants interstitially, is proposed as the mechanism responsible for the enlarged grains seen experimentally in (Ti/V/Cr/Mg)-doped systems. Mn- and V-doped UO₂ have been predicted to have higher uranium vacancy concentrations than the more widely used Cr-doped UO₂, leading to higher grain growth and fission gas diffusivity.

Appendix A.2. Introduction

UO₂ is the most widely used nuclear fuel due to its chemical stability, high melting point and radiation tolerance. The release of fission gas (Xe and Kr) creates technical issues during reactor operation. Fission gas release reduces the thermal conductivity of the fuel-cladding gap and increases the fuel rod pressure, which can lead to rod failure. Some incremental fuel concepts use a dopant during pellet sintering to promote grain growth. The aim is to increase the distance travelled (and time taken) during the rate limiting intra-granular diffusion step before rapid fission gas release from the grain boundaries. Cr [4–11], Nb [12–14], Mg [14–16], Ti [14, 17], and V [18] additives have all been identified as UO₂ grain enlargers. An additional benefit of enlarged grains is increased plasticity and thermal creep, which reduces mechanical interactions between the pellet and the metal cladding [1–3].

Generally grain growth can be expressed as:

$$\bar{G}^n - \bar{G}_0^n = t \cdot k_0 \exp\left(\frac{-Q}{k_B T}\right) \quad (\text{A.1})$$

where \bar{G}_0 and \bar{G} are the average grain size before and after annealing, respectively. T is the temperature, t is the annealing time, and k_B is the Boltzmann constant. n is a mechanism dependent parameter and various values have been suggested depending on interactions between

pores and grain boundaries [28–34]. The activation energy, Q , and pre-exponential, k_0 , are constants for the rate of the mechanism that governs grain growth. For ideal grain growth the dominant mechanism is bulk diffusion and $n = 2$.

Cr-doped UO_2 , in particular, is frequently studied. Liquid phase sintering due to the CrO eutectic has been identified in the literature as the primary mechanism for enhanced grain growth [4–9]. However, Bourgeois *et al.* [4] measured an increase in grain size as function of Cr content even if the sintering temperature was below the CrO eutectic melting temperature of 1950 K [19]. Furthermore, a maximum in grain size was observed at the Cr solubility limit [4], whereby further additions reduced the grain size. For sintering temperatures above the CrO liquid eutectic (1950 K [19]), Cr additions well in excess of the solubility limit further increase the grain size, which is almost certainly due to liquid phase sintering. Nonetheless, a peak in grain size at the Cr solubility limit is present for all temperatures. Similar observations have been made for grain size as a function of dopant content in Ti-doped UO_2 [17]. Furthermore, Mg-doped UO_2 also exhibits enlarged grains [16] despite the lack of a eutectic and the MgO melting point (3125 K) being well in excess of sintering temperatures. As such, an open question exists regarding the mechanism responsible below the dopant solubility limit and/or below the eutectic temperature.

The defect concentrations in $\text{UO}_{2\pm x}$ and doped $\text{UO}_{2\pm x}$ are highly dependent on oxygen partial pressure and temperature. The relative ease with which U^{4+} may oxidize to U^{5+} results in a low energy charge compensation mechanism for the negatively charged hyper-stoichiometric defects V_{U}''' and O_{i}'' . Consequently, UO_2 can be easily oxidized to UO_{2+x} or U_4O_9 , and even up to UO_3 through further oxidation to U^{6+} . However, it is not possible to reduce UO_2 to UO_{2-x} without heating the system to very high temperatures. Guéneau *et al.* [35] modelled the O/M ratio of $\text{UO}_{2\pm x}$ as a function of oxygen partial pressure and temperature by fitting to experimental data [36–50]. For a fixed oxygen partial pressure the O/M is found to reduce for increasing temperatures. A defect analysis [51] combining DFT defect energies with empirical potential vibrational entropy showed that uranium vacancies are suppressed at sintering temperatures due to reduction of UO_{2+x} to UO_2 . Since grain growth kinetics are tied to vacancy-mediated uranium diffusivity, this can be prevented to some extent by using hyper-stoichiometric UO_{2+x} powder [52, 53]. In this work mechanisms will be identified by which doping can also enhance uranium vacancy concentrations leading to high uranium diffusivity and faster grain growth kinetics via Equation A.1.

The role of Cr in solution for grain growth has often been dismissed due to its assumed preference for the 3+ valance state and for accommodation at the U site, i.e. Cr_{U}' in Kröger-Vink notation [54] as used throughout this paper. This would result in negatively charged substitutional defects, which would suppress the concentration of the similarly charged U vacancies, V_{U}''' . The possibility of Cr accommodation as a positively charged interstitial defect has been proposed in the literature [20–22], however, it is not born out in atomistic simulations, which have in the past been used to predict the substitutional defect as more favourable [20]. Although uranium interstitials have been predicted to kick out Cr substitutional defects into an interstitial site [23], this is not representative of equilibrium conditions. These calculations

used rigid Cr^{3+} models, which ignore the possibility that Cr can occupy multiple valence states given the d electrons in its outer shell. Cardinaels *et al.* [20] also concluded from comparison of XRD of Cr-doped UO_2 at room temperature with their atomistic calculations that Cr is in solution as a substitutional defect. However, vibrational entropy was not considered and may be important at the high sintering temperatures for UO_2 (1800-2200 K) and could lead to a change in the accommodation mechanism. Furthermore, the ability of dopants to access a wide range of valence states may allow solution mechanisms that were precluded from previous simulations. In particular, valence states higher than 4+ would create positively charged substitutional defects at the uranium site. Otherwise, any valence states that allow dopants to occupy the interstitial site would be equally significant in the creation of positively charged defects and the resulting increase in uranium vacancy concentrations.

In this work, we have combined vibrational entropies from empirical calculations and defect energies from DFT+ U within a defect analysis similar to that carried out on ThO_2 [55] and on $\text{UO}_{2\pm x}$ [51, 56]. Defect concentrations have been analysed for UO_2 doped with Cr and Al. It will be shown that Cr occupies lower valence states allowing it to access the interstitial site, whereas the high energy of Al reduction from 3+ to 2+ or 1+ prevents accommodation at the interstitial site. On this basis other dopants that can access lower valence states were also examined: the transition metals, Mn, Fe, Ti, and V, as well as the group 2 metal, Mg. The implications of increased uranium vacancy concentrations for enhanced grain growth and fission gas release are discussed.

Appendix A.3. Methodology

Defect calculations were carried out using the Vienna *ab initio* Simulation Package (VASP) [57–59]. The local density approximation (LDA) was applied to the exchange and correlation potential. The strongly correlated 5f electrons of uranium require the use of the LDA+ U functional of Lichtenstein *et al.* [60]. The wave function was calculated using the projector augmented wave (PAW) method with core electrons accounted for within the frozen core approximation [61, 62]. The values of $U=4.5$ eV and $J=0.51$ eV were taken from Dudarev *et al.* [63] in line with previous DFT studies on UO_2 [56, 64–67]. Unfortunately, the introduction of the U parameter creates the additional challenge of metastable electronic states, which must be treated carefully, for example, through occupation matrix control [68] or U -ramping [69] to ensure the ground state configurations are achieved. As a number of the dopants studied are transition metals, U and J parameters have been applied to the highly correlated d electrons as follows: $U=3.2$ eV and $J=0.0$ eV for Cr [70], $U=4.0$ eV and $J=0.0$ eV for Mn [71, 72], $U=4.0$ eV and $J=0.0$ eV for Fe [73], $U=3.0$ eV and $J=0.0$ eV for V [74], and $U=5.0$ eV and $J=1.0$ eV for Ti [75]. Spin-polarization was included with a 1- \mathbf{k} antiferromagnetic ordering giving a good description of the lowest energy non-collinear 3- \mathbf{k} ordering without including spin-orbit coupling, which due to computational cost prevents the use of sufficiently large supercells. This assumption is reasonable given that the Coulomb interaction was found to be 10-30 times higher than spin orbit coupling in 5f systems [76]. Furthermore, the 1- \mathbf{k} antiferromagnetic ordering gives a good approximation of the high temperature paramagnetic ordering [77].

All DFT calculations were carried out using a 96 atom supercell consisting of a $2 \times 2 \times 2$ expansion of the UO_2 fluorite unit cell. Here we apply the U -ramping method to the U ions by carrying out 20 ionic steps at constant volume for each value of U from $U=J=0.51$ eV to $U=4.5$ eV at 0.5 V increments. Subsequently, the ionic relaxation loop was converged to within 10^{-4} eV and the electronic relaxation loop to within 10^{-6} eV. Both ionic positions and cell parameters were relaxed during minimization. A plane-wave cut-off energy 500 eV was used. k -space integration was performed on a $2 \times 2 \times 2$ Monkhorst-Pack mesh [78] with Gaussian smearing of 0.05 eV. The interaction of charged defects with their periodic images has been corrected for through the Madelung energy [79, 80]. The potential alignment correction was applied to the defective lattice energy using the approach of Taylor and Bruneval [81].

Host defects included in our analysis are v_U , v_O , and O_i . Uranium interstitials have been shown previously to have negligible concentrations [51, 82] and have been omitted from this work. All charges ranging from neutral to formal have been included. Holes, U_U^\bullet , and electrons, U_U' , have been treated in the same fashion as other charged defects by adding or removing electrons from the perfect supercell, allowing for structural relaxation associated with localized defects. DFT calculations for the host defects were carried out as part of previous work on undoped UO_2 [51], while DFT calculations for dopant defects have been conducted here for the first time using the same methodology. The following ranges of dopant defect charges have been considered: Cr_U'' to $\bullet\bullet$, Cr_i^\times to $\bullet\bullet\bullet\bullet\bullet$, Mn_U'' to $\bullet\bullet$, Mn_i^\times to $\bullet\bullet\bullet\bullet\bullet$, Fe_U'' to $\bullet\bullet$, Fe_i^\times to $\bullet\bullet\bullet\bullet\bullet$, V_U'' to \bullet , V_i^\times to $\bullet\bullet\bullet\bullet$, Ti_U'' to \times , Ti_i^\times to $\bullet\bullet\bullet$, Al_U'' to \times , Al_i^\times to $\bullet\bullet$, Mg_U'' to \times , and Mg_i^\times to $\bullet\bullet$. The DFT defect energies are summarized in Tables A1 and A2 in the Appendix.

The phonon vibrational modes of perfect and defective UO_2 have been calculated using the General Utility Lattice Program (GULP) [83] using the the Busker potential [27]. A supercell consisting of a $4 \times 4 \times 4$ expansion of the fluorite unit cell was used for the calculation of phonon modes, v_n , which were then used in the following summation to determine the vibrational entropy:

$$S_{vib} = k_B \sum_{n=1}^{3N-3} \ln \left(\frac{h v_n}{k_B T} \right) + (3N - 3) k_B \quad (\text{A.2})$$

where k_B is the Boltzmann constant, v_n is the phonon frequency, T is the temperature, and h is Planck's constant. The derivative of equation A.2 with respect to volume, $\frac{dS}{dV}$, has also been calculated for each defective and non-defective supercell and combined with the experimental thermal expansion of UO_2 [84] to determine the vibrational entropy.

Due to the lack of empirical parameters for different dopant charge states, we have initially used the $\text{Cr}^{3+} - \text{O}^{2-}$ parameters to calculate the entropy of $\text{Cr}_i^{\bullet\bullet\bullet}$ and Cr_U' with both cell volumes and atomic positions relaxed. However, the change in volume of the UO_2 lattice due to Cr defects varies significantly for different charge states and has an impact through the derivative of UO_2 vibration entropy as a function of volume, $\left(\frac{dS}{dV} \right)_{\text{UO}_2}$. This should not be confused with the correction for thermal expansion described above. In order to capture the effect of the change in defect volume associated with a Cr defect with valence, q , the following correction

has been applied to the entropy of the Cr^{3+} defects:

$$S_{\text{Cr}^q} = S_{\text{Cr}^{3+}} + (V_{\text{Cr}^q} - V_{\text{Cr}^{3+}}) \cdot \left(\frac{dS}{dV} \right)_{\text{UO}_2} \quad (\text{A.3})$$

where $V_{\text{Cr}^{3+}}$ is the defect volume of a Cr^{3+} defect (i.e. $\text{Cr}_i^{\bullet\bullet\bullet}$ and Cr_U'), and where V_{Cr^q} is the defect volume of a Cr^q defect (e.g. if $q=2$ then $\text{Cr}_i^{\bullet\bullet}$ and Cr_U''). Defect volumes have been determined from geometry relaxation in DFT. Tables A3 and A4 in the Appendix summarize the defect vibrational entropies and the vibrational entropy of the reference lattices. The DFT defect volumes used to adjust for non-formal dopant charges (see equation A.3) are shown in Table A5 in the Appendix.

It was found that the difference in vibrational entropy between Cr and Al for a given defect (substitutional or interstitial) was less than 0.1 %. As such, for all dopants studied here (including Al for full consistency) we have used the interstitial and substitutional vibrational entropies calculated for Cr (summarized in Table A4 in the Appendix). Similarly the vibrational entropies of all dopant reference oxides have been assumed to be the same as for Cr. To account for different numbers of O atoms per metal dopant atom in some reference oxides (e.g. VO_2), the vibrational entropies for CrO and Cr_2O_3 have been extrapolated as a function of O/M. This is a first order approximation that may slightly affect predictions of the most stable reference phases at low temperature. However, it will be shown in Section Appendix A.4 that at the high temperatures relevant to sintering, MO and M_2O_3 reference oxides always dominate making this approximation suitable within the scope of this work, which focuses on grain growth at high temperatures.

The defect energy/entropy is the difference in energy/entropy between the defective and perfect supercells (see Tables A1-A4 in the Appendix). Using these the defect concentrations, c_i , are determined from an Arrhenius relationship:

$$c_i = m_i \exp \left(\frac{-\Delta G_f^i}{k_B T} \right) \quad (\text{A.4})$$

where m_i is the multiplicity, T is the temperature, and k_B is the Boltzmann constant. The free energy of defect formation is defined as:

$$\Delta G_f = \Delta E - T \Delta S_{\text{vib}} + \sum_{\alpha} n_{\alpha} \mu_{\alpha} + q_i \mu_e \quad (\text{A.5})$$

where the defect energy, ΔE , is determined from DFT and the defect entropy, ΔS_{vib} , is determined from empirical potentials. n_{α} and μ_{α} are the number of species, α , and chemical potential of species, α , respectively that have been added to the system. q_i is the charge of the supercell containing the defect and μ_e is the electron potential.

The total Gibbs free energy of UO_2 can be defined in terms of the chemical potentials per formula unit of the constituent species:

$$\mu_U(p_{\text{O}_2}, T) + \mu_{\text{O}_2}(p_{\text{O}_2}, T) = \mu_{\text{UO}_{2(s)}} \quad (\text{A.6})$$

where $\mu_U(p_{O_2}, T)$ and $\mu_{O_2}(p_{O_2}, T)$ are the chemical potentials of metal U and O_2 gas respectively. In a similar manner to the defect energies (ΔE in equation A.5) the energies used to calculate the chemical potentials are taken from DFT, while vibrational entropy contributions are determined using the Busker potential. DFT is well known to provide a poor description of the O_2 dimer. Here the approach of Finnis *et al.* [87] is employed, whereby referencing the experimental formation energy of the oxide removes use of DFT to obtain the chemical potential of O via:

$$\Delta G_f^{UO_2}(p_{O_2}^\circ, T^\circ) = \mu_{UO_2(s)} - \mu_{U(s)} - \mu_{O_{2(g)}}(p_{O_2}^\circ, T^\circ) \quad (A.7)$$

where $\Delta G_f^{UO_2}(p_{O_2}^\circ, T^\circ)$ is the experimental formation energy of UO_2 (-11.23 eV per UO_2 [88]). The temperature dependence of the O chemical potential is captured by using the ideal gas relations to extrapolate from $\mu_{O_{2(g)}}(p_{O_2}^\circ, T^\circ)$:

$$\mu_{O_{2(g)}}(p_{O_2}, T) = \mu_{O_{2(g)}}(p_{O_2}^\circ, T^\circ) + \Delta\mu(T) + \frac{1}{2}k_B T \log\left(\frac{p_{O_2}}{p_{O_2}^\circ}\right) \quad (A.8)$$

and the rigid-dumbbell ideal gas for $\Delta\mu(T)$ is defined as:

$$\Delta\mu(T) = -\frac{1}{2}(S_{O_2}^\circ - C_p^\circ)(T - T^\circ) + C_p^\circ T \log\left(\frac{T}{T^\circ}\right) \quad (A.9)$$

where $S_{O_2}^\circ = 0.0021 \text{ eVK}^{-1}$ is the molecular entropy at STP and $C_p^\circ = 7k_B = 0.000302 \text{ eVK}^{-1}$ is the constant pressure specific heat.

Using the framework discussed above the defect concentrations for a given set of conditions can be calculated by determining the electron potential, which is coupled to the charged defect formation energies, that ensures charge neutrality. The resultant defect concentrations can be expressed as a function of temperature or oxygen partial pressure and plotted to produce Brouwer diagrams. Generation of the Brouwer diagrams is done using the Defect Analysis Package [89]. For many of the dopants there are multiple reference oxides. The defect analysis was repeated using a different reference oxide each time for a given dopant, with the most stable reference state defined as that which has the lowest solubility in UO_2 for a given set of conditions. The following reference states have been considered: Cr_2O_3 , Cr_3O_4 , CrO , Mn_2O_3 , Mn_3O_4 , MnO , Fe_2O_3 , Fe_3O_4 , FeO , V_2O_5 , VO_2 , V_3O_5 , V_2O_3 , VO , TiO_2 , Ti_2O_3 , TiO , Al_2O_3 , and MgO . While V_2O_3 [90], Ti_2O_3 [91], Cr_2O_3 [92] and Al_2O_3 [93] all exhibit the corundum structure, Mn_2O_3 has the cubic bixbyite structure [94]. Fe_3O_4 has a cubic inverse spinel structure [95]. VO_2 [96] has distorted rutile-like monoclinic structure, V_3O_5 [97] exhibits the oxyvanite structure, and for V_2O_5 the structures listed in Ref. [98] were tested and the lowest energy used. TiO_2 exhibits the tetragonal rutile structure [99]. MgO , MnO , FeO , and VO all have the cubic rock salt structure [98, 100, 101]. However, for TiO the most stable structure is actually defective rock salt, $Ti_{1-x}O_{1-x}$. In this work the perfect rock salt energy of TiO is calculated and then adjusted using the energy of $Ti_{1-x}O_{1-x}$ relative to TiO from DFT calculations by Andersson *et al.* [102]. Although CrO only exists as a liquid, it has been treated as a rock salt solid here like the other oxides. It should be noted that above the eutectic temperature (1950 K) the free energy of the CrO liquid phase will be lower than for the theoretical rock salt. However, this is

near the upper temperature limit of our calculations and the solubility of Cr is still expected to increase as a function of temperature.

Appendix A.4. Results and discussion

Appendix A.4.1. Cr and Al doping

Figure A.2a shows the defect concentrations for Cr-doped UO_2 from 500 K to 2000 K with an O partial pressure of 10^{-20} atm. The black line in Figure A.2a represents x in $\text{UO}_{2\pm x}$ and the dip that occurs at about 1700 K is due to the transition from low temperature UO_{2+x} to high temperature UO_{2-x} . The v_{U}''' concentrations in the case of undoped UO_2 are also included using a dashed blue line. Given that our primary concern is the diffusivity of U due to its role in mass transport during grain growth and that U diffusion is vacancy assisted, the concentration of v_{U}''' in the doped case compared to the undoped case is key. At low temperatures Cr is predicted to be accommodated at the uranium site in very small concentrations, indicating low solubility. The low concentrations result in no change in v_{U}''' compared to the undoped case. Nonetheless, at low temperatures Cr^{3+} at the uranium site (Cr_{U}') is dominant relative to other valence states or Cr at other crystallographic sites. Although in the perfect fluorite lattice the uranium site is coordinated by 8 oxygen atoms, due to structural relaxation Cr exhibits 6-fold coordination when substituting the uranium ion (see Figure A.2a). This result is validated by x-ray absorption fine structure (EXAFS) spectroscopy experiments on Cr-doped UO_2 at room temperature, which also shows Cr^{3+} with octahedral symmetry coordinated by 6 oxygen anions [9, 10]. Furthermore, we predict Cr-O and U-O bond lengths of 2.13 Å and 2.38 Å, respectively, in reasonable agreement with experimental values of 2.02 Å and 2.36 Å, respectively [10].

For fixed oxygen partial pressure as the temperature increases the conditions become more reducing and the degree of excess oxygen decreases. Consequently, the concentrations of hyperstoichiometric defects, O_{I}'' and v_{U}''' , decrease. Although the concentration of v_{U}''' in undoped UO_2 decreases, increased sintering kinetics with temperature still occur due to faster hopping of the remaining v_{U}''' . However, in the case of Cr-doped UO_2 , significant quantities of Cr are dissolved at the interstitial site at high temperature. The Cr^{1+} ion is dominant at the interstitial site and the octahedron symmetry also seen for the substitutional site is maintained. Dopant accommodation at the interstitial site is a key result that, although hypothesized [20–22], has not been shown in previous work. Without accounting for the ability of the dopant to change valence state (e.g. from 3+ to 2+ to 1+) this mechanism would not have been identified. It is interesting that the charge effects of the interstitial defect seem to drive cations into a lower charge state, overcoming the size effects associated with the larger ionic radius of low valence ions. In this context it is worth noting the high stability of the O^{2-} interstitial in UO_2 , which exhibits a greater ionic radius and lower valence than Cr^{1+} . Nonetheless, it is possible that for larger dopants or host systems with a smaller interstitial site the size effects might limit the transferability of this mechanism. As the $\text{Cr}_{\text{I}}^{\bullet}$ concentration exceeds that of $\text{U}_{\text{U}}^{\bullet}$ it becomes the dominant positively charged defect, which results in increased concentrations for all negatively defects in the system. Most importantly, the v_{U}''' concentration for Cr-doped UO_2 exceeds that for undoped UO_2 for $T > 1775$ K and does so by over an order of magnitude at $T = 2000$ K,

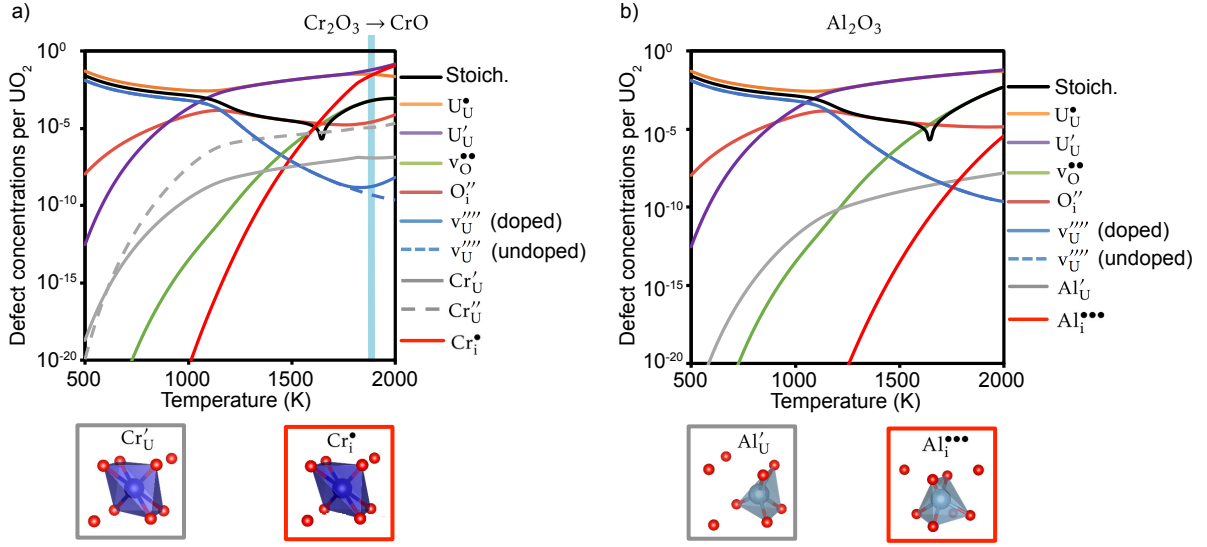


Figure A.2: Defect concentrations in a) Cr-doped and b) Al-doped $\text{UO}_{2\pm x}$ as function of temperature (500-2000 K) for an O partial pressure of 10^{-20} (atm). The most stable reference oxide for a given temperature is indicated above the figures. The crystallographic coordination of Cr and Al at the uranium and interstitial sites is shown below the figures.

which would allow enhanced U mass transport and enlarged grains during sintering (see equation A.1). Note that upon cooling some Cr might be quenched in solution and is predicted to transition from the interstitial site to the U site and from Cr^{1+} to Cr^{3+} , which is consistent with experiments [9, 10]. Alternatively, due to insolubility at low temperatures Cr_2O_3 precipitates might form, which has also been observed [4, 11]. The ultimate balance between precipitation and quenching would depend on the cooling rate and Cr mobility.

Bourgeois *et al.* [4] showed that enhanced sintering can be achieved by Cr doping at 1800 K. The Cr interstitial mechanism proposed here can explain enhanced sintering at 1800 K (see Figure A.2a), whereas the lowest possible temperature for the CrO liquid eutectic is 1950 K. Furthermore, by investigating grain size as a function of Cr content Bourgeois *et al.* found a peak at around the Cr solubility limit (700-1000 ppm) for all temperatures, and at temperatures above the eutectic they also found a secondary peak for Cr content well in excess of the solubility limit. We propose that formation of $\text{Cr}_\text{i}^\bullet$ and its effect on v_U''' concentrations is responsible for the observed peak in grain size at the Cr solubility limit. For higher Cr content: i) if above the CrO eutectic temperature one would observe a secondary peak due to liquid phase sintering occurring in parallel to the interstitial mechanism or ii) if below the eutectic temperature solid secondary phases would pin grain boundaries and reduce grain size.

Starkly different behaviour is predicted for Al-doped UO_2 (see Figure A.2b). Whereas Cr can transition to Cr^{1+} upon occupying the interstitial site at high temperature, Al does not. Al also prefers a 5-fold symmetry at both sites (see Figure A.2b). It appears that there is a preference of

the interstitial site for a 1+ valence cation and the reluctance of Al to exhibit lower valence states seems to prohibit the formation of significant concentrations of Al interstitials. Consequently, $\text{Al}_i^{\bullet\bullet\bullet}$ never approaches similar concentrations to the dominant positively charged defect, U_U^\bullet , and no impact on $v_U^{\prime\prime\prime}$ concentrations is predicted for Al-doped UO_2 compared to undoped UO_2 . This is in agreement with experiment where Al is shown not to enhance grain growth [18, 21]. Rather the formation of solid Al_2O_3 can inhibit grain growth by pinning [18]. There is evidence [8] that combinations of Al- and Cr-doping has an improved effect on grain size, however, this is beyond the scope of our point defect analysis.

The underlying difference between Al and Cr derives from their electronic structure. Cr is a transition metal, which means it can form stable ions with only a partially filled d shell. As a result the different valence states of Cr lie close in energy to each other, enabling it to transition to the lower charge states (i.e. 1+) favored by the interstitial site. On the other hand, Al has a 3s² 3p¹ outer shell giving a strong preference to lose all 3 electrons in the outer shell and making the transition to charge states below 3+ unfavourable, which reduces the interstitial solubility at sintering temperatures. This opens the possibility that other transition (d electron) metals, which have chemistry that is not prohibitive of the lower charge states favored by the interstitial site, could enhance grain size through the same mechanism. It is important to select elements within this group that have small ionic radii so that the favorable charge effects of low valence interstitials is not overcome by size effects that would prefer the substitutional site.

Appendix A.4.2. Other transition metals: Ti, V, Mn, and Fe

The same defect analysis was carried out for some transition metals other than Cr. Figure A.3a shows that Mn behaves in a similar fashion to Cr, although there are now 3 important reference states (Mn_2O_3 , Mn_3O_4 , and MnO) compared to 2 for Cr (Cr_2O_3 and CrO). The transition from the substitutional defect to the interstitial defect occurs at 1400 K for Mn compared to 1500 K for Cr. The solubility of Mn_i^\bullet is approximately 2 times that of Cr_i^\bullet in the high temperature regime (>1800 K), resulting in 3.5-5 times greater $v_U^{\prime\prime\prime}$ concentrations. It is, therefore, anticipated that Mn-doped UO_2 will exhibit larger grains than Cr-doped UO_2 after sintering by utilising a higher Mn content in solution at interstitial sites [103]. Similarly to Cr, Mn is predicted to exhibit octahedral symmetry coordinated by 6 O at both the interstitial and substitutional sites (see Figures A.2a and A.3a).

Figure A.3b shows that even though $\text{Fe}_U^{\prime\prime}$ transitions to Fe_i^\bullet it is predicted to result in just a slight increase in the $v_U^{\prime\prime\prime}$ concentrations compared to undoped UO_2 up to 2000 K, which is due to the relative insolubility of Fe. Therefore, Fe is not expected to provide improved sintering with respect to Cr-doped UO_2 , although grain size may be enhanced compared to undoped UO_2 for high sintering temperatures. We also note that Fe exhibits different coordination at both the uranium and interstitial sites compared to Mn and Cr. $\text{Fe}_U^{\prime\prime}$ has a 4-fold coordination asymmetric with respect to the perfect lattice uranium site. Fe_i^\bullet exhibits 8-fold coordination at the interstitial site (see Figure A.3b). Despite the lower solubility the interstitial site still seems to enforce the 1+ charge state forming Fe_i^\bullet .

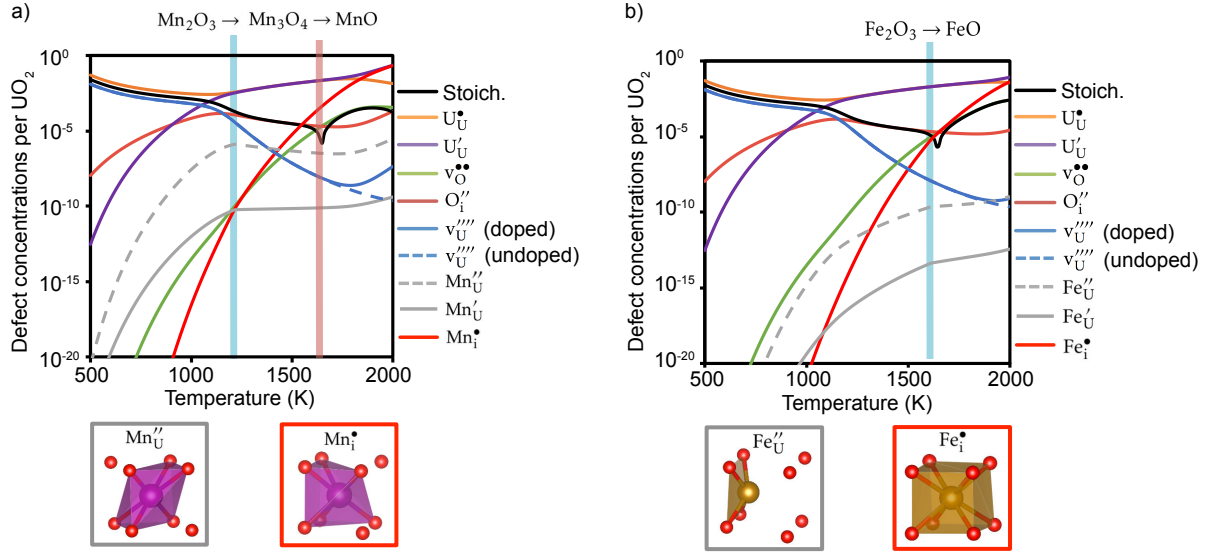


Figure A.3: Defect concentrations in a) Mn-doped UO_2 and b) Fe-doped UO_2 as function of temperature (500–2000 K) for an O partial pressure of 10^{-20} (atm). The most stable reference oxide for a given temperature is indicated above the figures. The crystallographic coordination of Mn and Fe at the uranium and interstitial sites is shown below the figures.

In agreement with experimental observation [14, 17, 18], Figure A.4 shows that enlarged grains can be expected in V- and Ti-doped UO_2 through the interstitial mechanism. V_U' and $\text{V}_\text{i}^\bullet$ have 5-fold coordination with significant deviation of V from the perfect lattice sites. Of all the dopants studied in this paper V exhibits the greatest increase in $\text{V}_\text{U}^{\prime\prime\prime}$ concentration. In fact the enhancement of negatively charged defects and suppression of positively charged defects is sufficient to reverse the transition from UO_{2+x} to UO_{2-x} , such that a second dip at stoichiometry (black line) occurs. For Ti the dominant defects are Ti_U' and $\text{Ti}_\text{i}^{\bullet\bullet}$ both with 8-fold coordination at the perfect lattice uranium and interstitial sites respectively. It is interesting that for the Ti interstitial the 2+, rather than 1+, valence state is favourable. While this again highlights a preference for lower charge states at the interstitial site, it indicates that there is a difference in the electronic structure of Ti that tips the balance in favour of 2+. For all other transition metal dopants studied (Cr, Mn, and Fe) the transition from 1+ to 2+ still leaves the d orbital partially filled (less favourable), whereas for Ti this transition leaves the d orbital empty (more favourable) with the outer shell consisting of just s electrons. Additionally, Ti being the larger of the transition metal dopants might be more favorable in a higher charge state that would reduce its volume and allow it to better fit the interstitial site. The results for the 2+ valence of the Ti interstitial demonstrates the ability of 2+ charged ions to occupy the interstitial site and motivates the investigation of group 2 metals (Section Appendix A.4.3). Ainscough et al. [17] showed that below the titania-urania eutectic melting temperature (1875 K) grain growth peaks at the solubility limit, above which grain growth was inhibited by titania precipitates. Above

the eutectic melting temperature further enhancement could be achieved above the solubility limit through liquid phase sintering. This supports our prediction that the interstitial dopant mechanism is important up to the solubility limit for Ti UO₂ and/or below the eutectic melting temperature.

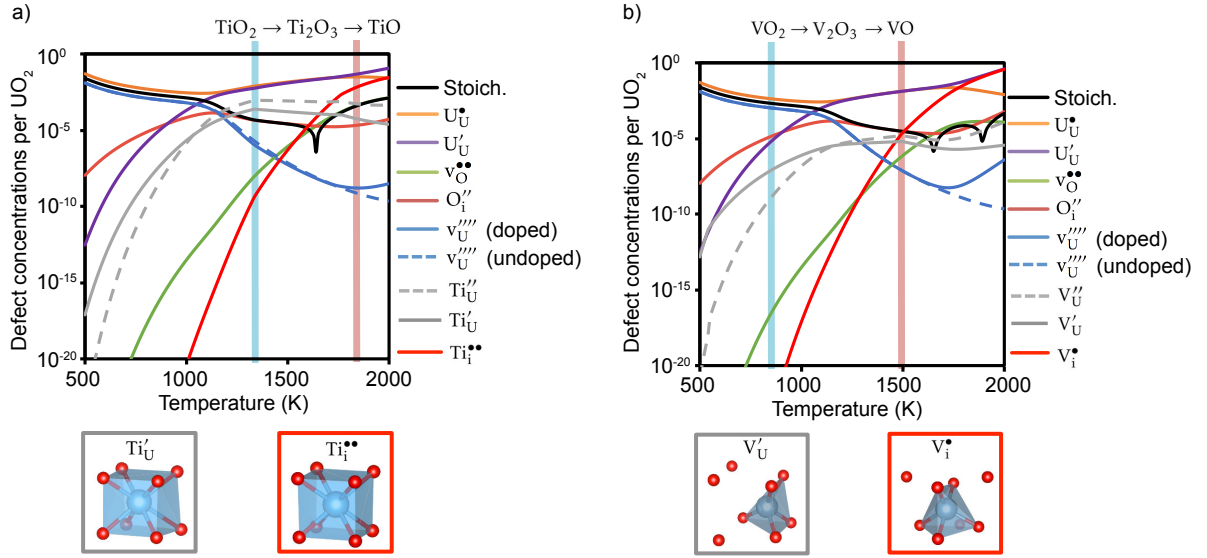


Figure A.4: Defect concentrations in a) Ti-doped UO₂ and b) V-doped UO₂) as function of temperature (500-2000 K) for an O partial pressure of 10⁻²⁰ (atm). The most stable reference oxide for a given temperature is indicated above the figures. The crystallographic coordination of Ti and V at the uranium and interstitial sites is shown below the figures.

Appendix A.4.3. Group 2 metals: Mg

Given the importance of the lower valence states (e.g. 2+ for Ti) for accommodation at the interstitial site, group 2 elements are natural candidates for enhanced grain growth. Figure A.5 shows that Mg does indeed occupy the interstitial site in much higher concentrations than Al, although not to the same extent as Cr, Mn, Ti or V. For all dopants studied here (except Al) the monoxide is the most stable reference state at sintering temperatures. For Mg the high stability of MgO may contribute to limited solubility at high temperature, despite its natural affinity for the 2+ valence state associate with Mg_i^{••}. Regardless, our results predict that Mg can be used to enhance grain size for high sintering temperatures as has also been shown experimentally [14–16].

Similar to other dopants, at low temperatures Mg is predicted to occupy the U site. In contrast to the transition metals and Al, the solubility of Mg_U^{''} at low temperatures is relatively high. Consequently, when the concentration of the negatively charged Mg_U^{''} approaches that of other negatively charged defects (v_U^{'''} and O_i[']) it begins to suppress the v_U^{'''} concentration. Unlike the other dopants studied, which dissolve directly onto the interstitial site, Mg transitions from the substitutional to the interstitial site. Experimental work by Fujino *et al.* [16] showed

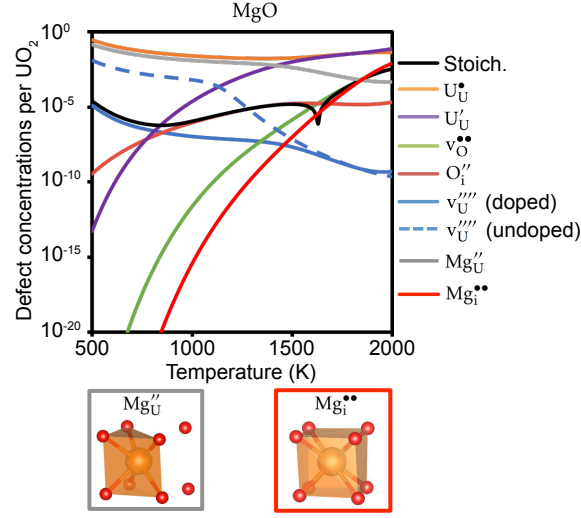


Figure A.5: Defect concentrations in Mg-doped $\text{UO}_{2\pm x}$ as function of temperature (500-2000 K) for an O partial pressure of 10^{-20} (atm). The most stable reference oxide for a given temperature is indicated above the figures. The crystallographic coordination of Mg at the uranium and interstitial sites is shown on the right hand side.

that Mg can be accommodated at both the uranium and interstitial sites with a bias towards the interstitial at high temperatures, in line with our calculations.

Appendix A.4.4. Discussion

Throughout the results section it has become apparent that the ability of a dopant to occupy lower valence states (1+ or 2+) underpins the formation of positively charged interstitial defects. The relative stability of the interstitial and the substitutional dopants is key for the ability of dopants to introduce positive charge to system. This is examined by fitting Arrhenius functions to the ratio of interstitials to substitutional defects, $\frac{[X_i]}{[X_U]}$, taken from the defect concentrations (summed over all charge states) shown in Figure A.2-A.5. There are three distinct temperature regimes for $\frac{[Cr_i]}{[Cr_U]}$ to which we have fitted three Arrhenius functions, in Figure A.6. The transition between two regimes is governed by a change in the dominant charge compensating mechanism. In the case of Cr for low temperatures $V_U^{\bullet\bullet}$ and U_U^\bullet dominate, for intermediate temperatures U_U^\bullet and U_U^\bullet dominate, and for high temperatures Cr_i^\bullet and U_U^\bullet dominate. The same analysis has been carried out for all the dopants and the coefficients for each regime are summarized in Table A.2. The three regimes for Cr can be generalized to Mn, Ti, V, and Fe, such that the transition between the low and intermediate regimes is independent of the dopant and occurs at the same temperature (1080 K) but the transition from the intermediate to the high regime is commensurate with the temperature at which enhancement of $v_U^{\bullet\bullet}$ concentrations occurs for a given dopant. For Al the high temperature regime does not exist because $Al_i^{\bullet\bullet}$ is never a dominant defect. On the other hand, Mg replaces $V_U^{\bullet\bullet}$ as the dominant negatively

charged defect in the low temperature regime. The resulting transition to the intermediate (U'_U and U_U^\bullet dominated) regime now occurs at 1430 K.

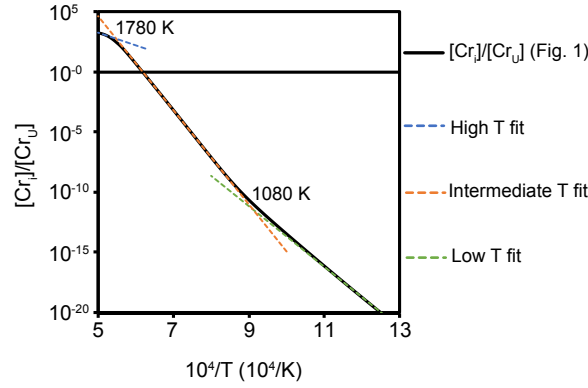


Figure A.6: The fraction of Cr interstitial defect concentrations to substitutional defect concentrations (summed over all charge states), $\frac{[Cr_i]}{[Cr_U]}$, calculated from Figure A.2a) is shown by the solid black line. The dashed lines indicate Arrhenius fits to $\frac{[Cr_i]}{[Cr_U]}$ in three different regimes. The parameters for the Arrhenius fits are shown in Table A.2.

It is this extrinsic positive charge created by interstitial formation that increases the concentrations of all negatively charged host defects including the v_U'''' concentration, which increases the U diffusivity. Figure A.7a shows the v_U'''' concentrations as a function of temperature in undoped and (Mg/Al/Ti/V/Cr/Mn/Fe)-doped UO_2 from Figures A.2-A.5 but zoomed in at temperatures relevant to sintering and the centerline fuel pellet temperature. It is more clearly seen in Figure A.7a that Fe and Mg only slightly enhance the v_U'''' concentrations, i.e. with respect to undoped UO_2 at 2000 K Fe and Mg enhance v_U'''' by a factor of 3 and 2, respectively. This is relatively limited when compared to Mn and Cr, which enhance v_U'''' concentrations by 1 – 2 orders of magnitude.

Enlarged grains are considered to increase plasticity (through the Hall-Petch effect [104, 105]) and reduce fission gas release (by increasing the distance of the rate limiting intra-granular diffusion step). Assuming that initial grain size is much smaller than the final grain size ($\bar{G} \gg \bar{G}_0$) and ideal (i.e. bulk diffusion dominated) grain growth, Equation A.1 can be expressed as:

$$\bar{G}^2 = t \cdot k_0 \exp\left(\frac{-Q}{k_B T}\right) \quad (A.10)$$

For diffusion dominated grain growth, uranium diffusion is the rate limiting step, whereby $k_0 \exp\left(\frac{-Q}{k_B T}\right)$ is proportional to the uranium diffusivity, which is in turn proportional to the concentration of v_U'''' assuming the mobility of an individual vacancy is unchanged. It is possible, therefore, to express the average grain size of doped UO_2 , \bar{G}_{doped} , relative to that of undoped

Table A.2: The relative stability of interstitial vs substitutional dopants is summarized by fitting an Arrhenius function ($A \exp \frac{-B}{k_b T}$) to the data for $\frac{[X_i]}{[X_U]}$ (summed over all charges) from Figures A.2-A.5 $X = \text{Cr, Al, Mn, Fe, Ti, V, Mg}$

Dopant, X (Temperature range)	A (no units)	B (eV)
Cr (600-1080 K)	3.049×10^{11}	4.993
Cr (1080-1780 K)	1.425×10^{24}	7.754
Cr (1780-2000 K)	3.362×10^8	2.094
Al (600-1080 K)	1.305×10^9	5.188
Al (1080-2000 K)	9.000×10^{22}	8.255
Mn (600-1080 K)	1.144×10^{13}	4.993
Mn (1080-1700 K)	1.477×10^{24}	6.866
Mn (1700-2000 K)	1.943×10^8	1.268
Fe (600-1080 K)	1.149×10^{13}	3.817
Fe (1080-1880 K)	1.432×10^{24}	6.298
Fe (1880-2000 K)	4.627×10^{13}	2.396
Ti (600-1080 K)	1.909×10^{13}	5.582
Ti (1080-1760 K)	2.787×10^{23}	7.923
Ti (1760-2000 K)	9.459×10^{10}	3.503
V (600-1080 K)	1.403×10^{14}	5.011
V (1080-1730 K)	3.215×10^{24}	7.250
V (1730-2000 K)	6.001×10^6	1.155
Mg (600-1430 K)	1.763×10^{12}	5.115
Mg (1430-1980 K)	3.279×10^{20}	7.457
Mg (1980-2000 K)	1.786×10^{15}	5.382

UO_2 , $\bar{G}_{undoped}$, as:

$$\frac{\bar{G}_{doped}}{\bar{G}_{undoped}} = \sqrt{\frac{[v_U''']_{doped}}{[v_U''']_{undoped}}} \quad (\text{A.11})$$

where $[v_U''']_{doped}$ and $[v_U''']_{undoped}$ are the uranium vacancy concentrations for doped and undoped UO_2 shown in Figure A.7a. $\frac{\bar{G}_{doped}}{\bar{G}_{undoped}}$ is shown in Figure A.7b. Note that for non-ideal grain growth mechanisms $n > 2$ and the extent of grain enhancement in real life might be not as great as shown in Figure A.7b. The predictions made here for uranium vacancy concentrations can be fed into sintering simulations for more complete predictions of grain growth.

An implication of Cr and Mn dopants is that they result in increased v_U''' concentrations at reactor operating temperatures, which is an important parameter for the diffusivity of fission gas [106–108]. Hence, it is expected that the bulk fission gas diffusivity would be increased (especially in the central region of the fuel) effectively competing with larger grain size for the amount of fission gas ultimately released from grain boundaries. This hypothesis is supported by the observation of Killeen *et al.* [7] that Cr-doped UO_2 has higher Kr diffusivity than undoped UO_2 at 1775 K. Furthermore, from fission gas release measurements Massih [6] reports

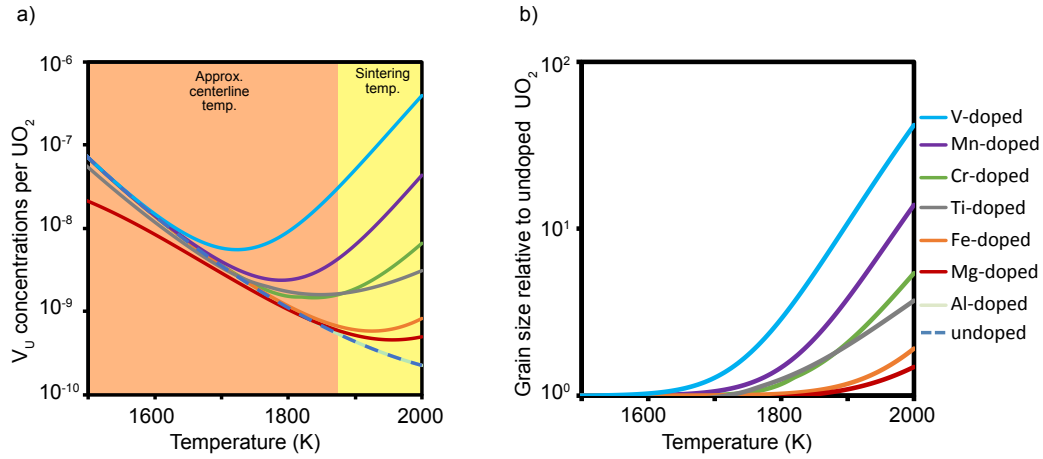


Figure A.7: a) Comparison of the v_U''' concentrations in undoped and (Mg/Al/Ti/V/Cr/Mn/Fe)-doped UO_2 at temperatures relevant to the fuel centreline and for sintering with an O partial pressure of 10^{-20} (atm). b) The grain size enhancement with respect to undoped UO_2 assuming diffusion dominated grain growth.

that above 1500 K Cr-doped UO_2 has higher Xe diffusivity than undoped UO_2 (the converse is true below 1500 K), this is commensurate with our prediction of the transition between Cr substitutional and interstitial defects. Kashibe and Une [22] also report that Al- and Mg- have no effect on Xe diffusivity. Une *et al.* [53] report that additions of 0.5 wt% Nb and 0.2 wt% Ti result in Xe diffusivity enhancement of factors of 50 and 7 respectively, supporting our prediction of a common interstitial-based v_U''' enhancement mechanism for a wide range of dopants. The relationship between enhanced fission gas diffusivity and enlarged grains, and the integrated role on fission gas release, is a complicated issue that must be addressed by longer length and time scale simulations not to mention additional experiments. Nonetheless, as a consequence of enhanced fission gas diffusivity we do not expect the full benefit of enlarged grains to be attained. Similarly for V-doped UO_2 even greater grain enlargement is expected compared to Ti-, Cr- and Mn-doped UO_2 , however we predict that fission gas diffusivity will also be greater. Regardless, large grain size in doped UO_2 would still provide enhanced plasticity with benefits to the mechanical interactions between the pellet and the cladding.

The transferability of this interstitial mechanism across a wide range of transition and group 2 metal dopants opens the possibility that it could also be transferable across a range of similar host systems. The transferability of this mechanism depends on the favorable low charge state effect of the doping ion overcoming the potential size effect limitations associated with the interstitial site and larger radii of low valence ions. We anticipate this work will form the basis for future studies on a wider body of materials. For example, the role of dopants in grain growth of doped CeO_2 is unclear [109–111].

Appendix A.5. Conclusions

Enlarged UO_2 grain size is thought to provide better nuclear fuel performance through increased plasticity and improved fission gas retention. Dopants have been widely used to provide enhanced grain growth during sintering. While liquid phase sintering has been often touted in the literature, there are experimental observations that lend themselves to the idea that there may be an additional grain growth mechanism during sintering. By re-examining the role of dopants in solution in UO_2 with relaxed assumptions of dopant valence state, we predict that an interstitial solution mechanism contributes to enhanced grain size in a number of doped systems. In particular, this mechanism increases v_{U}''' concentrations, thus, resulting in higher U diffusivity during sintering (i.e. faster grain growth).

The defect analysis was carried out using DFT defect energies and empirical potential vibrational entropy on the solution of Cr, Al, Mn, Fe, Ti, V, and Mg into UO_2 as a function of temperature. Negatively charged substitutional defects were predicted to dominate for all dopants over a large temperature range. The concentrations of these defects are sufficiently low for Cr, Al, Mn, Fe, Ti, and V as to not affect the v_{U}''' concentrations compared to undoped UO_2 . Mg on the other hand forms Mg_{U}'' at significant enough concentrations to suppress v_{U}''' concentrations at low temperatures.

At temperatures relevant to sintering, all dopants studied were predicted to form 1+ or 2+ charged interstitial defects at different concentrations depending on the dopant. V-doped UO_2 was predicted to have the highest solubility at the interstitial site followed by Mn, Ti and Cr. Consequently, Ti, V, Cr, and Mn greatly enhance the v_{U}''' concentrations compared to undoped UO_2 . Fe and Mg also enhance the v_{U}''' concentration but to a lesser extent, while Al has no effect.

Enhanced v_{U}''' concentrations in doped fuel will also increase fission gas diffusivity at operating temperatures (especially near the centerline). The extent to which enhanced diffusivity competes with larger grains for fission gas retention is unclear and requires further consideration. However, we have shown an important aspect of the problem, which is that the same mechanism governs both grain growth kinetics and fission gas diffusivity.

Appendix A.6. Acknowledgements

We would like to thank ST Murphy at Lancaster University for his support using the Defect Analysis Package [89]. This work was funded by the U.S. department of Energy, Office of Nuclear Energy, Nuclear Energy Advanced Modeling Simulation (NEAMS) program. Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under Contract No. DE-AC52-06NA25396.

Appendix A.7. Supplementary information

Here we provide the defect data from DFT and empirical potential calculations that were used in the defect analysis carried out in the main body of the paper. The DFT lattice energies

have been corrected for the interactions between the charged defect with its periodic images through the Madelung energy such that [79, 80]:

$$E_{\infty} = E_L + \frac{q^2 \alpha}{2\epsilon L} \quad (\text{A.12})$$

where E_{∞} is the lattice energy in the dilute limit, $E(L)$ is the lattice energy in a supercell of length L , and q is the supercell charge. $\alpha = 2.837$ is the Madelung constant of a point charge q placed in a homogeneous background charge $-q$ and $\epsilon = 22$ is the dielectric constant taken from experiment [112]. A potential alignment correction to the defect lattice energies, ΔV , due to the shift in band structure of the defective supercell with respect to the perfect supercell was calculated as [81]:

$$\Delta V = \langle v_{KS}^{bulk} \rangle - \langle v_{KS}^{defect} \rangle \quad (\text{A.13})$$

where $\langle v_{KS}^{bulk} \rangle$ and $\langle v_{KS}^{defect} \rangle$ are the average Kohn-Sham potentials in the perfect and defective supercells respectively. The charge and potential alignment corrected defect energies are summarized in Table A1 for host defects and in Table A2 for dopant defects.

Table A1: DFT defect energies for host (U and O) defects with various charges [51]. The energies have been corrected for the interaction of the charged defect with its periodic images using Equation A.12 and corrected for potential alignment using Equation A.13. The DFT energy of perfect UO_2 per formula unit is 31.935 eV

Effective charge	Defect energy (eV)						
	-4	-3	-2	-1	0	+1	+2
Non-defective (eV)	-	-	-	10.070	0.000	-8.566	-
V_O (eV)	-	-	-	-	12.024	2.243	-7.321
O_i (eV)	-	-	11.546	2.703	-5.945	-	-
V_U (eV)	53.336	44.774	36.294	27.798	19.467	-	-

The values of S_{vib} for various defects has been calculated from equation A.2 with the phonon modes predicted by the Busker potential [27]. The derivative of equation A.2 with respect to volume, $\frac{dS}{dV}$, for the defective and perfect supercells has been used to adjust for the experimental thermal expansion [84]. The difference between the perfect and defective supercells, ΔS_{vib} , is summarized in Tables A3 and A4 alongside the vibrational entropy of the reference oxides. Table A5 shows the defect volumes for interstitial and substitutional Cr defects with various charge states. The difference in volume relative to the Cr^{3+} defects has been used with $\left(\frac{dS}{dV}\right)_{\text{UO}_2} = 0.341 \text{ k}_B/\text{\AA}^3$ to modify the defect entropies in Table A4 to determine the entropy for non-formally charged defects (equation A.3).

Table A2: DFT defect energies for dopant defects with various charges. The energies have been corrected for the interaction of the charged defect with its periodic images using Equation A.12 and corrected for potential alignment using Equation A.13

Effective charge	Defect energy (eV)								
	-2	-1	0	+1	+2	+3	+4	+5	+6
Cr _i	-	-	-3.691	-13.778	-22.885	-31.354	-39.775	-48.384	-56.460
Cr _U	26.232	17.287	8.894	0.498	-8.021	-	-	-	-
Al _i	-	-	0.122	-10.001	-19.781	-29.563	-	-	-
Al _U	28.607	18.861	10.526	-	-	-	-	-	-
Mn _i	-	-	-2.724	-12.797	-21.494	-29.953	-38.293	-46.655	-55.106
Mn _U	28.106	19.539	8.981	3.721	-2.706	-	-	-	-
Fe _i	-	-	-2.925	-13.068	-21.693	-30.093	-38.735	-47.106	-55.608
Fe _U	28.400	19.856	11.338	2.817	-5.499	-	-	-	-
Ti _i	-	-	-3.615	-13.751	-23.533	-32.080	-40.629	-	-
Ti _U	25.619	16.135	7.548	-	-	-	-	-	-
V _i	-	-	-4.559	-14.521	-23.830	-32.469	-41.012	-49.240	-
V _U	26.123	16.533	8.022	-0.370	-	-	-	-	-
Mg _i	-	-	1.046	-8.891	-18.559	-	-	-	-
Mg _U	29.652	21.158	12.620	-	-	-	-	-	-

Table A3: Using the Busker potential [27], the change in lattice entropy of UO₂ due to a host defect (ΔS_{vib}) and the vibrational entropy of the UO₂ lattice per formula unit, which is used to calculate the chemical potential of the U atoms

T (K)	Lattice entropy UO ₂ (k_B) [51]	Defect entropy for host defects (ΔS_{vib})					Reaction entropy	
		v _O (k_B) [51]	O _i (k_B) [51]	v _U (k_B) [51]	U _U [•] (k_B) [51]	U _U ' (k_B) [51]	SD (k_B)	OFP (k_B)
400	7.785	-0.245	8.305	2.410	-1.195	4.309	9.108	7.959
600	11.531	-1.544	9.705	1.085	-1.149	4.243	9.528	8.060
800	14.219	-2.109	10.752	0.103	-1.103	4.177	9.343	8.160
1000	16.328	-3.242	11.606	-0.686	-1.057	4.110	9.157	8.262
1200	18.069	-3.872	12.339	-1.353	-1.010	4.043	8.972	8.364
1400	19.559	-4.419	12.989	-1.936	-0.964	3.976	8.785	8.467
1600	20.863	-4.903	13.577	-2.458	-0.917	3.908	8.590	8.570
1800	22.026	-5.341	14.119	-2.933	-0.870	3.840	8.410	8.673
2000	23.078	-5.742	14.624	-3.371	-0.822	3.771	8.222	8.882

Table A4: Using the Busker potential [27], the change in lattice entropy of UO_2 due to a Cr defect (ΔS_{vib}) and the vibrational entropy of the reference lattices (per Cr atom) used in the calculation of the chemical potential of the dopant atoms is shown per formula unit

T (K)	Reference oxide entropy per Cr		Defect entropy for Cr defects (ΔS_{vib})	
	Cr_2O_3 (k_B)	CrO (k_B)	Cr'_{U} (k_B)	$\text{Cr}^{\bullet\bullet\bullet}_{\text{i}}$ (k_B)
400	4.059	5.221	1.360	8.767
600	7.126	7.672	1.132	10.114
800	9.309	9.418	0.903	11.108
1000	11.001	10.778	0.673	11.909
1200	12.405	11.892	0.442	12.588
1400	13.588	12.839	0.209	13.184
1600	14.618	13.662	-0.024	13.718
1800	15.529	14.391	-0.259	14.205
2000	16.347	15.046	-0.495	14.656

Table A5: The change in lattice volume due to geometry optimization of Cr defects with different charge states, q . The difference in volume with respect to the formally charged defects (shown in braces) is used in conjunction with $\left(\frac{dS}{dV}\right)_{\text{UO}_2} = 0.341 \text{ k}_B/\text{\AA}^3$ to adjust the entropy for Cr defects with non-formal charges (equation A.3)

Cr valence (q)	Defect	Defect volume (\AA^3)	Defect	Defect volume (\AA^3)
0	-	-	$\text{Cr}^{\times}_{\text{i}}$	9.76 (32.88)
I	-	-	$\text{Cr}^{\bullet}_{\text{i}}$	-3.02 (20.10)
II	Cr''_{U}	13.66 (15.90)	$\text{Cr}^{\bullet\bullet}_{\text{i}}$	-15.80 (7.32)
III	Cr'_{U}	-2.24 (0.00)	$\text{Cr}^{\bullet\bullet\bullet}_{\text{i}}$	-23.12 (0.00)
IV	$\text{Cr}^{\times}_{\text{U}}$	-12.94 (-10.70)	$\text{Cr}^{\bullet\bullet\bullet\bullet}_{\text{i}}$	-36.27 (-13.15)
V	$\text{Cr}^{\bullet}_{\text{U}}$	-26.48 (-24.24)	$\text{Cr}^{\bullet\bullet\bullet\bullet\bullet}_{\text{i}}$	-48.22 (-25.10)
VI	$\text{Cr}^{\bullet\bullet}_{\text{U}}$	-37.13 (-34.89)	$\text{Cr}^{\bullet\bullet\bullet\bullet\bullet\bullet}_{\text{i}}$	-59.71 (-36.59)

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